thermometer in freezing mercury, consistency of their observations demands that such a calibration yield the value —38.83° for the Callendar temperature of the mercury freezing point. This value is of the order of 0.04° higher than that universally obtained with resistance thermometers of the strain-free type and the existence of such a difference relatively so near the ice point had not previously been observed, even for a flat-coil type of thermometer.

Summary

A simple modification of the Callendar equation used in platinum-resistance thermometry above 0° is given, which will express accurately the resistance of platinum as a function of temperature on the thermodynamic scale throughout the range 0°C. to —190°. The application of the new equation requires but a single calibration point below zero. Recalculations of data on resistance thermometers at low temperatures obtained by the Reichsanstalt and the Bureau of Standards are made, showing that the modified equation expresses the experimental results within the error of observation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THEORY OF CERTAIN ELECTROMETRIC AND CONDUCTIMETRIC TITRATIONS

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In the familiar hydrogen-electrode titration curves (e.m.f. *vs.* volume of added acid or base) a point of inflection usually occurs in the vicinity of the end-point. When both the acid and the base are strong it is rather obvious that this inflection must occur exactly at the end-point. If there is a difference in strength of acid and base, or if both are weak, the exact coincidence of inflection-point and end-point is no longer obviously necessary or probable. And if either the acid or base is sufficiently weak the point of inflection does not appear at all. The limiting strength of acid or base necessary for the appearance of the inflection and the extent of its divergence from the end-point under various conditions are, therefore, questions which must be considered in the more general applications of the method. Similar questions appertain to the "break" in conductivity titration curves. Some years ago occasion was taken to study these problems analytically in connection with an investigation then in progress. Since that time the results of this study have often been found to be of value to investigators making use of these methods, and also in teaching. It has, therefore, been decided to offer a summary of them for publication, together with an outline of the procedures by which they were obtained.

The only work now in the literature, so far as is known to the writer, which bears directly upon any of the points considered in this paper is the approximate calculation by Kolthoff[1] of the limiting strength of acid or base which it is practicable to titrate by the conductimetric method.

Hydrogen-Ion Concentration during Titration

Under certain conditions to be discussed the concentrations of the substances involved in a titration of an acid with a base are connected in the most general case by the six simultaneous equations given below. In these equations the formulas of the acid and base are assumed to be HA and BOH, respectively, and the concentrations of the various substances are represented by their formulas in parentheses. K_W, K_A and K_B represent the dissociation constants of water and of the acid and base, respectively. The number of moles of acid originally present is denoted by c and the number of moles of base added by V. The equations then are,

$$\begin{array}{llll} (\mathrm{H}^+)\,(\mathrm{OH}^-) = K_W & (1) & (\mathrm{H}^+) + (\mathrm{B}^+) = (\mathrm{OH}^-) + (\mathrm{A}^-) & (4) \\ (\mathrm{B}^+)\,(\mathrm{OH}^-)/(\mathrm{BOH}) = K_B & (2) & (\mathrm{A}^-) + (\mathrm{HA}) = c & (5) \\ (\mathrm{H}^+)\,(\mathrm{A}^-)/(\mathrm{HA}) = K_A & (3) & (\mathrm{B}^+) + (\mathrm{BOH}) = \mathrm{V} & (6) \end{array}$$

The equations are written assuming that the acid and base follow the mass law and the salt is completely dissociated. They apply strictly, therefore, only in quite dilute solutions, although in more concentrated solutions they no doubt lead to approximately correct results. The further assumption is made in these equations that a constant volume of 1 liter is maintained throughout the titration. This condition is realizable, but not fulfilled in ordinary titrations. Results in the latter will be closely represented by the same equations, however, if the constant c is allowed to represent the concentration of salt at the end-point.

Combination of Equations 1–6 leads to a general relation between the amount of added base and the hydrogen-ion concentration, as follows.

$$\mathrm{V} = [K_A\,c/(K_A + (\mathrm{H}^+)) + K_W/(\mathrm{H}^+) - (\mathrm{H}^+)]\,[K_W/K_B(\mathrm{H}^+) + 1] \qquad (7)$$

The appearance of V as an explicit function of (H^+) in this equation adds difficulty to the later work, although not to the extent that would make desirable an attempt to transform to an (approximate) expression giving (H^+) as a function of V.

At the end-point V is equal to c. This condition introduced into (7) leads to an expression for the hydrogen-ion concentration at the end-point of any titration, which we may cast in the following form.

$$K_A{}^{-1}\,(\mathrm{H}^+)^4 + (K_W K_A{}^{-1} K_B{}^{-1} + cK_A{}^{-1} + 1)\,(\mathrm{H}^+)^3 + K_W\,(K_B{}^{-1} - K_A{}^{-1})\,(\mathrm{H}^+)^2 - K_W(K_W K_A{}^{-1} K_B{}^{-1} + cK_B{}^{-1} + 1)\,(\mathrm{H}^+) - K_W{}^2 K_B{}^{-1} = 0 \qquad (8)$$

Position of Inflection-Points in Hydrogen-Electrode Titration Curves

In titrations with the hydrogen electrode it is usual to plot as ordinate the e.m.f. of the cell used against the volume of the solution of base added.

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[1] Kolthoff, *Z. anorg. Chem.*, **111**, 1 (1920).

The latter quantity is proportional to the number of moles, V, of base in the preceding and the former is a linear function of the so-called Sörensen (P_{H}) value. Determination of the location of inflection-points in the $P_{\mathrm{H}} - \mathrm{V}$ curve will, therefore, suffice for the present purpose. The P_{H} value will be here defined, considering activity and concentration equal, as

$$P_{\mathrm{H}} = -\log_{10} (\mathrm{H}^+) \tag{9}$$

The condition for inflection-points in the titration curve then is that the second derivative of P_{H} with respect to V be zero. By combination of derivatives obtained from Equation 7 with those from Equation 9 it is possible to express $d^2P_{\mathrm{H}}/d\mathrm{V}^2$ as a function of hydrogen-ion concentration. On equating the resulting expression to zero an equation of condition is obtained which may be written as follows.

$$K_{\mathrm{A}}^{-3}(\mathrm{H}^+)^6 + 3K_{\mathrm{A}}^{-2}(\mathrm{H}^+)^5 + K_{\mathrm{A}}^{-1}(3-cK_{\mathrm{A}}^{-1} - K_{\mathrm{W}}K_{\mathrm{A}}^{-2})\ (\mathrm{H}^+)^4 + [1 + cK_{\mathrm{A}}^{-1} + 3K_{\mathrm{W}}K_{\mathrm{A}}^{-2} - 4K_{\mathrm{W}}K_{\mathrm{A}}^{-1}K_{\mathrm{B}}^{-1}(cK_{\mathrm{A}}^{-1} + K_{\mathrm{W}}K_{\mathrm{A}}^{-2})]\ (\mathrm{H}^+)^3 - 3K_{\mathrm{W}}K_{\mathrm{A}}^{-1}(1 + cK_{\mathrm{B}}^{-1} + 4K_{\mathrm{W}}K_{\mathrm{A}}^{-1}K_{\mathrm{B}}^{-1})\ (\mathrm{H}^+)^2 - K_{\mathrm{W}}(1 + cK_{\mathrm{B}}^{-1} + 12K_{\mathrm{W}}K_{\mathrm{A}}^{-1}K_{\mathrm{B}}^{-1})\ (\mathrm{H}^+) + 4K_{\mathrm{W}}^2K_{\mathrm{B}}^{-1} = 0 \tag{10}$$

Comparison of Equations 10 and 8 giving the hydrogen-ion concentration at the inflection and end-points, respectively, shows that they cannot be made identical and will not always be satisfied by the same values of (H^+). It follows that in the general case the inflection-point does not occur exactly at the end-point. To find to what extent the positions of the two differ in any given case the procedure is to substitute the particular values of the constants and solve for (H^+) in Equations 8 and 10, and then by substituting the value found from (10) in Equation 7 calculate the corresponding value of V. To investigate the question as to the limiting strength of acid or base necessary to produce an inflection in the curve, the dissociation constants K_{A} or K_{B} are successively decreased until it is found that no real roots, in the range of hydrogen-ion concentration possible in a titration, occur in Equation 10. The disappearance of these roots marks the disappearance of the inflections in the curve. By these methods a number of typical cases of common interest have been investigated. A resumé of the results is given below.

When acid and base are both strong (completely dissociated), their dissociation constants, K_{A} and K_{B}, are infinite. Equations 8 and 10 both reduce, then, to the equation

$$(\mathrm{H}^+) = \sqrt{K_{\mathrm{W}}} \tag{11}$$

In this case the end-point and inflection point coincide and are independent of the concentrations employed.

The case of strong base and weak acid is covered by making K_{B} alone equal to infinity. It is then found that with $c = 1$, an inflection occurs if $K_{\mathrm{A}} = 10^{-11}$ but not if $K_{\mathrm{A}} = 10^{-12}$. With $c = 10^{-3}$, the preceding values of K_{A} are increased to 10^{-8} and 10^{-9}, respectively. The failure of the inflection to appear seems more remarkable when it is considered that in the first of the above cases, for example, with $c = 1$ and $K_A = 10^{-12}$, only about 10% of the acid would remain undissociated (that is, only 10% of the salt would be hydrolyzed) at the end-point. Further, with acid of strength but little more than sufficient to produce an inflection, the inflection- and end-points are appreciably different in position. The inflection occurs, in this case, before the end-point is reached. At the inflection-point (H^+) is approximately 5% larger and V about 0.3% smaller than at the end-point, these figures remaining nearly unchanged for values of c between 10^{-8} and 1. These discrepancies decrease rapidly as the strength of acid is increased.

For simplicity in studying the titration of weak acids with weak bases the examples taken were limited to those of equal strength. On placing $K_B = K_A$ in Equations 7, 8 and 10, and substituting numerical values it is found that with $c = 1$, inflections are obtained if K_A and K_B are as large as 10^{-6} but not if they are 10^{-7}. For $c = 10^{-3}$, these values are increased to 10^{-5} and 10^{-6}, respectively. The inflection- and end-points again do not occur exactly together; (H^+) at the inflection-point when $c = 10^{-3}$ and $K_A = 10^{-5}$ is 2% larger than at the end-point. This corresponds, however, to only 0.04% in V. The titration is, therefore, essentially accurate in this case.

Conductivity Titrations

It will be recalled that in conductivity titrations use is made of the fact that under the usual circumstances an abrupt change in direction occurs in the neighborhood of the end-point in curves obtained by plotting the specific conductance of the solution against the amount of acid or base added during titration. This change is occasionally so sharp as to be referred to as a "break." The curves are, however, perfectly continuous and the break used to mark the end-point is in reality only the point of maximum curvature. The location of the point of maximum curvature in a number of the cases previously chosen as typical was investigated by the methods and with the results outlined below.

Keeping the original Equations 1–6, with their attached conditions, one new variable and a new equation enter when conductivity is considered. Letting κ represent the specific conductance of the solution, the equation is

$$K = \lambda_{H^+}(H^+) + \lambda_{OH^-}(OH^-) + \lambda_{B^+}(B^+) + \lambda_{A^-}(A^-) \qquad (12)$$

In this equation the quantities denoted by λ, with the subscripts corresponding to the individual ions, are the equivalent conductances of the ions (assumed to be independent of concentration), divided by 1000, since κ is the specific conductance and the volume of the solution is assumed to be 1 liter. Combination of Equation 12 with Equations 1–6 gives the conductivity as a function of hydrogen-ion concentration.

The expression resulting is

$$\kappa = (\lambda_{H^+} - \lambda_{B^+})\,(H^+) + K_W(\lambda_{OH^-} + \lambda_{B^+})/(H^+) + cK_A(\lambda_{B^+} + \lambda_{A^-})/(K_A + (H^+)) \tag{13}$$

The curvature, ρ, of the $\kappa - V$ curve is given by

$$\rho = \frac{\dfrac{d^2\kappa}{dV^2}}{\left[1 + \left(\dfrac{d\kappa}{dV}\right)^2\right]^{3/2}} \tag{14}$$

This equation may be shown to be equivalent to

$$\rho = \frac{\dfrac{d^2V}{d(H^+)^2} - \dfrac{d^2\kappa}{d(H^+)^2} \times \dfrac{dV}{d(H^+)} \Big/ \dfrac{d\kappa}{d(H^+)}}{\left(\dfrac{d\kappa}{d(H^+)}\right)^2 \left[1 + \left(\dfrac{dV}{d(H^+)}\right)^2 \Big/ \left(\dfrac{d\kappa}{d(H^+)}\right)^2\right]^{3/2}} \tag{15}$$

The derivatives in the last expression may be obtained as functions of (H^+) by differentiations in Equations 7 and 13. It is then possible also to obtain $d\rho/dV$ as a function of (H^+) and by equating to zero to solve for (H^+) at the "break." The algebraic expressions resulting in this process are, however, very complex. It appeared simpler in practise, therefore, to find by substituting numerical values calculated for the derivatives in Equation 15 at various hydrogen-ion concentrations, the value of the latter variable at which ρ reaches a maximum under the conditions of interest. It is then possible from (7) to fix the value of V at which the break occurs and to compare this value with that at the end-point.

The constants λ_{B^+} and λ_{A^-}, for which numerical values must be substituted among others in this process, are not the same in all titrations. But the conductances of the positive and negative ions in different salts differ from each other much less than from those of hydrogen or hydroxyl ion. To obtain results roughly representative of most of the ordinary titrations, rounded values of equivalent conductances were used in this work as follows: $\Lambda_{H^+} = 350$, $\Lambda_{OH^-} = 200$, $\Lambda_{B^+} = \Lambda_{A^-} = 50$ reciprocal ohms. Appropriate substitution for K_A and K_B in the typical cases were made as in the preceding. The results of the calculations follow.

In the strong acid—strong base titration the maximum curvature occurs very close to the neutral point. The difference from the end-point does not exceed a few thousandths of 1% in V.

In the strong base—weak acid titration a maximum in curvature still exists, with $c = 10^{-3}$, for acids with dissociation constants as small as 10^{-10}, though not at 10^{-11}. The limits respecting strength of acid are, therefore, wider than for the hydrogen-electrode inflections, where the corresponding limit in K_A is 10^{-8}. The maximum curvature in the above case, however, occurs some 11% before the end-point is reached. With $c = 10^{-3}$ and $K_A = 10^{-8}$ in the conductivity titration, results are comparable with the corresponding electrode example. The maximum curvature then occurs about 0.5% before the end-point is reached. It is seen, therefore, that as the strength of acid is increased the "break" and the true end-point rapidly approach each other.

The final examples studied relate to the case where acid and base are both weak. It was ascertained that with $K_A = K_B = 10^{-6}$ the "break" occurs about 2% before the true end-point, both at concentrations corresponding to $c = 10^{-3}$ and to $c = 1$.

From a comparison of these results it appears that, while the maximum of curvature persists in conductivity-titration curves over wider ranges of acid strength than does the inflection point in hydrogen-electrode curves, in these extended ranges the indication of the end-point is in error by rather large amounts. In ranges of acid strength where both methods are applicable, the indications of the hydrogen electrode are somewhat nearer the true end-point than those from conductivity.

Summary

In this paper the location of the end-points as obtained in hydrogen electrode and conductivity titrations is investigated mathematically for varying concentrations and strengths of acid and base in certain simple typical cases. It is concluded that the indication of the end-point by the hydrogen-electrode method is exactly corerct only when a strong acid and a strong base are titrated against each other. It is shown that with either the acid or base weak there are limiting values of the dissociation constants beyond which no indication of the end-point is obtained at all. These limits are given. The greatest inaccuracies in end-point occur when there is the greatest difference possible in the strength of acid and base. The largest error in the end-point in any of the cases studied is 5% in the hydrogen-ion concentration and 0.3% in the amount of base added. In the cases of common interest the error is much less than this.

In no case studied was the indication of the end-point in conductivity titrations found to be exactly correct. It is very closely so in the strong acid—strong base case. Under comparable conditions as to strength of acid and base the indications in other cases are slightly more in error than those of the hydrogen electrode. The maximum of curvature, or the "break," in conductivity curves persists over wider ranges of the dissociation constant of acids and bases used than does the inflection in curves by the hydrogen-electrode method. In these extended ranges, however, the point of maximum curvature differs very considerably from the true end-point.

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